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How Hg isotope source signatures can be overprinted by biogeochemical processes in the subsurface of contaminated legacy sites

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Contaminated legacy sites can represent a long-term source from which mercury (Hg) is released to waterbodies, soils and the air and present a potential risk to local human and environmental health. The understanding of Hg biogeochemistry at such sites, and in the environment in general, still poses large challenges using the currently available and established analytical methods. This holds especially true for the investigation of Hg species transformation processes. The combination of multiple methods allows for a more in-depth characterization of environmental samples and can help to overcome weaknesses of individual methods and therefore improve the interpretation of mechanisms involved in the (re-)mobilization of Hg. Our recently published dataset [1] from two contaminated legacy sites demonstrates the benefit but also some limitations of integrating Hg stable isotope analysis as an additional dimension to complement analyses of Hg concentrations and binding forms. The isotopic composition of Hg can be characteristic for distinct source material as well as the extent of mass-dependent and mass-independent fractionation processes which have affected the investigated environmental sample, opening up the possibility to trace certain sources and biogeochemical processes.

In our study we present Hg stable isotope data for solid-phase digests and extracts from drill cores, complemented by analyses of Hg binding forms determined by sequential extractions and pyrolytic thermal desorption, as well as groundwater analyses downgradient from the site.

The results show that the initially highly soluble source of Hg from timber treatment by HgCl₂ (cyanization) transforms to more recalcitrant Hg forms during the leaching through the soil column and the transport of Hg to groundwater. In a first step the initial sorption of Hg to the soil matrix leads to kinetic fractionation and with ongoing filling of sorption sites to equilibrium fractionation. Both processes lead to a preferential sorption of lighter isotopes. The labile Hg transported downwards in the soil column therefore has a more positive $\delta^{202}\text{Hg}$ and thus the underlying layers exhibit a more positive $\delta^{202}\text{Hg}$ than the highly contaminated top layers. This is supported by isotopic results of sequential extracts which show a general trend of more positive $\delta^{202}\text{Hg}$ values for easily leachable Hg (F1+F2) compared to more tightly bound forms of Hg (F3+F4).

The transport in the groundwater contamination plume is reflected in progressively more positive liquid phase $\delta^{202}\text{Hg}$ values compared to the solid phase as Hg is transported away from the source area. This indicates the importance of sorption of liquid phase Hg to solid phase Hg for the retention of Hg in the aquifer and the retardation of the Hg contamination plume even in matrices with very low organic matter content (<1%). The findings of our study emphasize the importance of carefully considering the overprinting of Hg isotope source signatures by biogeochemical processes in the interpretation of data from legacy sites.

[1] McLagan, D.S., Schwab, L., Chen, L., Pietrucha, J., Kraemer, S.M., Biester, H., 2022. Demystifying mercury geochemistry in contaminated soil-groundwater systems with complementary mercury stable isotope, concentration, and speciation analyses. *Environ. Sci. Process. Impacts*. <https://doi.org/10.1039/D1EM00368B>